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Effect of particle size on the mechanical properties of poly(vinylchloride)-copper particulate composite

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The effect of particle size ratios on tensile strength, tensile modulus, impact strength, Vickers hardness and transverse rupture strength of particulate PVC–Cu composite has been studied. The strength values reach a maximum at a particular metal loading where the formation of a segregated network is believed to occur. This critical metal loading shifts towards lower values with increasing polymer-to-metal size ratios. The mean free path calculated from the proposed model is found to be same in all metal loadings, corresponding to strength maxima irrespective of the particle size ratios. A correlation between strength properties and the mean free path has been suggested.

1. Introduction

In the early work on particulate composites, various theoretical models [1–6] have been proposed to predict the mechanical properties. Nielsen and others [1–3] put emphasis on the volume fraction of the filler and mode of packing, while Hojo *et al.* [4], Altar [5] and Baldwin [6] found different linear and non-linear relationships between strength of the composite and the particle size of the filler. Landon *et al.* [7] showed the importance of adhesion between filler and the matrix phase in explaining mechanical behaviour of the composite. Similar observations have been made by Brassell and Wischmann [8].

Turner and co-workers [9, 10] introduced the concept of segregated network formation in metal loaded polymeric systems. They discussed the effect of segregated distribution of nickel on the mechanical properties of PVC. Similar observations have been made in this laboratory in the case of poly(methyl methacrylate)–Cu composites [11]. The increased hardness of the composites had been attributed to the increased coalescence of the polymer particles under compaction conditions and by activation due to heat transfer by the metal particles. In the present investigation we have studied the effect of the particle size ratios of polymer to metal particles on the mechanical properties of PVC–Cu composites.

2. Experimental procedure

2.1. Materials

Commercially available PVC powder sieved out into 2 fractions of average particle sizes 180 μm and 128 μm were used. The specific gravity of the polymer powder was found to be 1.4. The molecular weight, as determined by viscosity measurement, was found to be 6.0×10^4, and glass transition temperature, as determined by a quartz dilatometer, was 85° C.

Copper powder used in the experiment was an electrolytic powder. The fraction of finer particle size ($< 45\,\mu$m) was separated into various fractions by an air elutriation method. The average particle size was measured by a Fisher Model 95 Sub-Sieve Sizer. The various fractions had particle sizes 12, 7, 4.3 and 3.7 μm.

The particles used for different polymer-to-metal size ratios are tabulated in Table I.

2.2. Preparation of composites

Polymeric and metallic powders were thoroughly mixed by tumbling until a homogeneous mixture was obtained. The mixture was then compacted in

TABLE I Particle size ratio of the composites

Average particle diameter of PVC ($2r_p$) (μm)	Average particle diameter of electrolytic copper powder ($2r_m$), as determined by Fisher sub-sieve sizer (μm)	r_p/r_m
128	12.0	11
128	7.0	18
180	7.0	26
128	4.3	30
128	3.7	35

a steel cylindrical die at 450 kg cm^{-2} and a temperature of 135° C for 15 min and the composites so formed were ejected out of the die at 60 to 70° C. The composites were easily machinable.

2.3. Mechanical testing

Notched specimens for impact tests were machined according to ASTM D256 (Method A). The impact strength was measured on a cantilever beam Izod-type impact machine (Avery 6702, Birmingham) with a hammer speed of 8 ft sec^{-1}.

Tensile tests on dumbell-shaped specimens were carried out using an Instron testing machine (model TMM). The cross-head speed used on a nominal cross-sectional area of 5 mm x 3 mm was 0.05 cm min^{-1}.

Transverse rupture strength was measured with a Universal testing machine (Trevel work, Düsseldorf, model UPM 4). The load was applied at a rate of 2.5 cm min^{-1}.

Vickers hardness was measured with a Heckart hardness testing machine using a diamond indenter at a load of 5 kg.

All the mechanical properties were measured at ambient temperature (30 to 32° C).

3. Results

3.1. Mechanical properties

Fig. 1 shows the representative stress–strain curves for PVC with 0%, 2% and 5% by volume of metal fillers. The typical necking rupture [12] of pure PVC (Fig. 1a) is retained at low volume per cent of the filler (Fig. 1b) but is replaced by a completely brittle mode of fracture at high metal concentration (Fig. 1c). The introduction of the filler also leads to a drastic drop in ductility and the value for elongation at fracture drops down from about 30% to 4 to 8% for PVC–Cu composites. Similar observations have been made by Kusy and Turner [10] in their studies on the PVC–Ni system.

Tensile modulus, tensile strength and transverse rupture strength as a function of metal concentration are presented in Figs. 2, 3 and 4. A strengthening effect of the matrix due to the introduction of copper is evident from the fact that the peak tensile modulus and tensile strength values show an increase of about 70% from that of the base value of PVC. In all cases the properties pass through a maxima at a particular metal loading. This critical metal loading, however, shifts towards lower values with increasing r_p/r_m ratios.

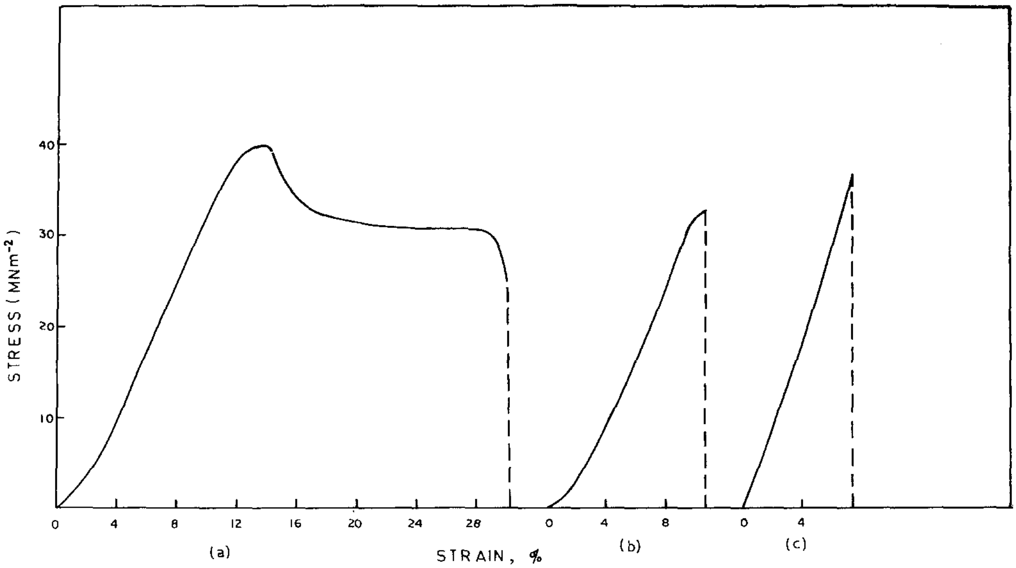


Figure 1 Stress–strain plot of (a) pure PVC, (b) composite with 2 vol% metal loading, and (c) composite with 5 vol% metal loading.

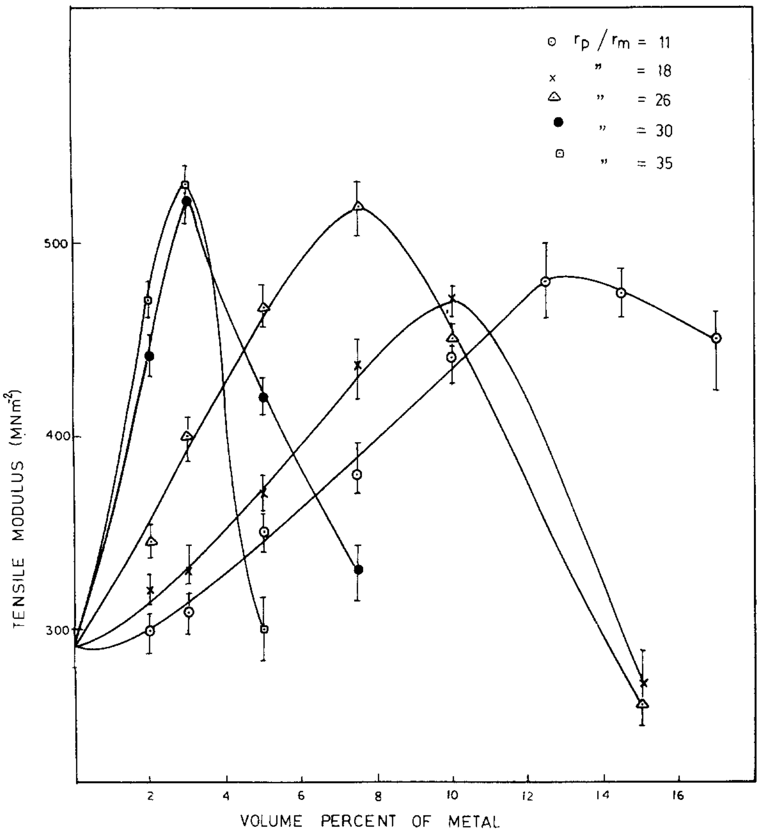


Figure 2 Tensile modulus as a function of metal concentration for different particle size ratios.

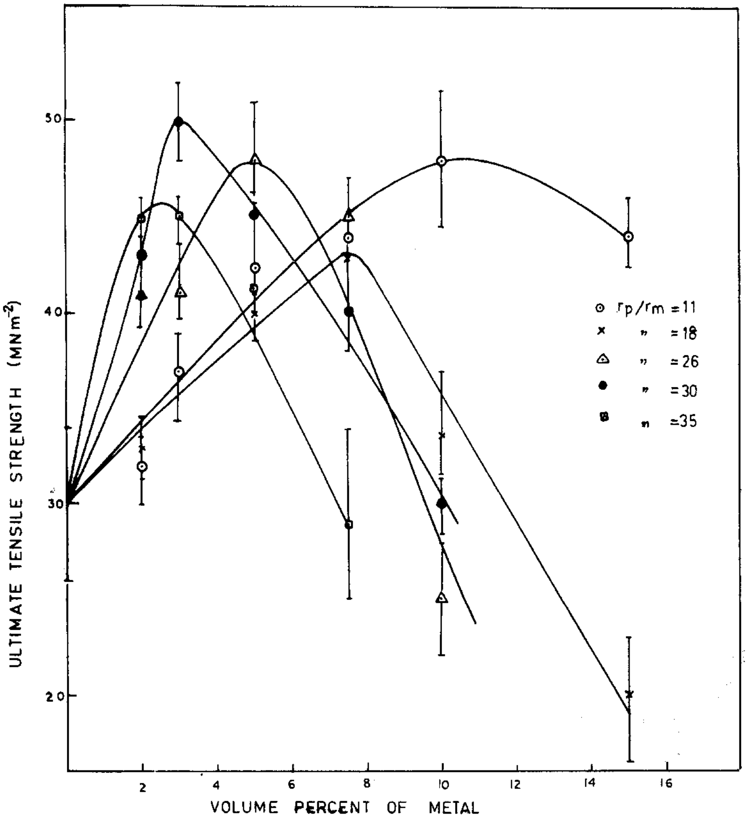
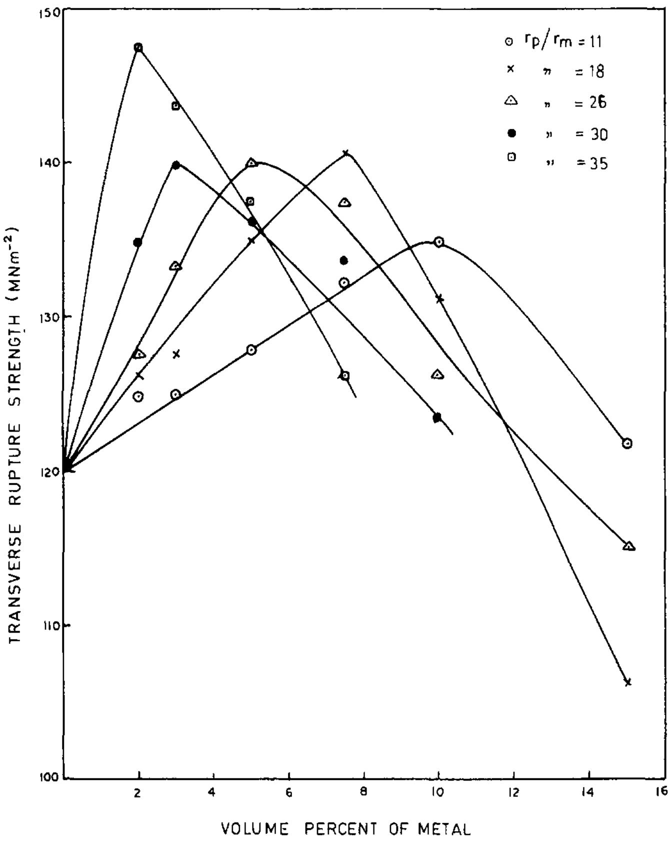


Figure 3 Ultimate tensile strength as a function of metal concentration for different particle size ratios.

Figure 4 Transverse rupture strength as a function of metal concentration for different particle size ratios.



The critical metal loadings as referred to above occur at almost the same values as where sudden falls in electrical resistivity were observed earlier [13]. The maxima in the mechanical properties and the drastic fall in electrical resistivity for a particular r_p/r_m is believed to be due to the formation of infinite chains of metal particles (segregated network) in the polymer matrix. The photomicrograph in Fig. 5 shows that the formation of a segregated network which is very much dependent on particle size ratios at a constant metal loading [13] as well as on metal concentration at a constant particle size ratio [11].

Figure 5 Optical photomicrograph (90 ×) at 25 vol% metal loading.

In order to find a correlation between the impact strength and the metal loading, samples with r_p/r_m = 18 were tested and the results are plotted in Fig. 6. The impact value at 7.5% metal loading was found to increase by about 60% of that of pure polymer. Vickers hardness, in general, was found to increase with increasing metal concentration (Fig. 7) and no correlation between hardness and particle size ratios were observed.

The fracture surfaces of various blends as revealed by a scanning electron microscope (Cambridge Stereoscope S$_4$10) studies are shown in Fig. 8. It is clearly seen that at metal loadings below the maximum the fracture propagates through the matrix, as is evident from the dimpled structures (Fig. 8a), while beyond the strength maximum the fracture moves through a demarcated segregated network of metallic particles around the planar polymer faces (Fig. 8b).

4. Discussion

The strength maxima obtained at a particular metal loading in the present investigations has also

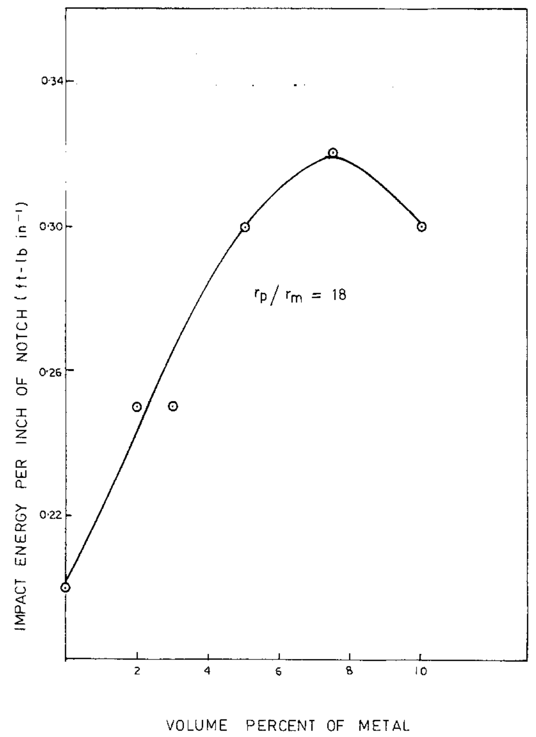


Figure 6 Impact strength as a function of metal concentration at $r_p/r_m = 18$.

been confirmed earlier in PMMA–Cu system [11]. Similar observation has been made by Gurland *et al.* [14] in metallic system and this had formed the basis of the theory of particle reinforced composites as postulated by Broutman and Krock [15]. The postulated theories predict that for these composites strengthening depends upon the particle size, as well as the mean free path between the particles. The relationship shows that the strength should be proportional to the inverse of the square root of the mean free path. There is a critical limit of the closeness of particles beyond which there is a catastrophic drop in strength due to easy propagation of cracks [6]. A model proposed earlier by the present authors [13] has been utilized in the present work in calculating the mean free path between metal particles for these composites. The model proposes the formation of a network of copper particles over the faces of polymer cuboids piled up in a three dimensional grid. Fig. 9 shows the basic features of the proposed model.

At any volume per cent V_p of the polymer the number of metal particles (n) attached to the surface of a polymer particle is given by (V_m/V_p)

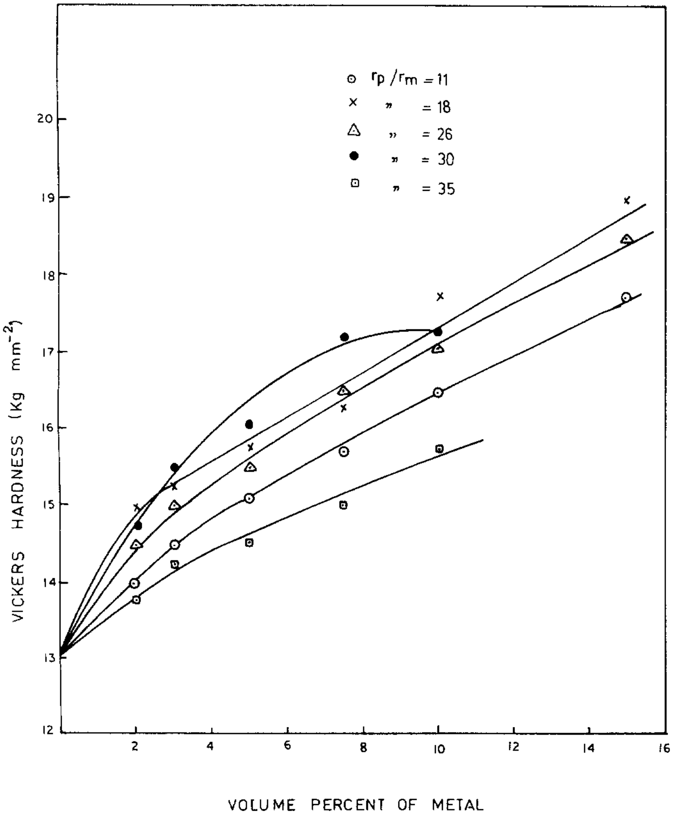


Figure 7 Vickers hardness as a function of metal loading for different particle size ratios.

(r_p^3/r_m^3) where r_p and r_m are the radii of polymeric and metallic particles and $V_m = 1 - V_p$. However, it is assumed that the polymer particles after compaction assume a cubic shape, the number of metal particles on an edge of the unit composite cube of dimension r_e being

$$\left[\frac{1}{6}\frac{r_p^3}{r_m^3}\frac{V_m}{V_p}\right]^{1/2},$$

and the length of the edge uncovered is given by

$$r_e - 2r_m\left[\frac{1}{6}\frac{r_p^3}{r_m^3}\frac{V_m}{V_p}\right]^{1/2}$$

Hence the mean distance between the metallic particles, (d_m) is given by

$$d_m = \frac{r_e - 2r_m\left[\frac{1}{6}\frac{r_p^3}{r_m^3}\frac{V_m}{V_p}\right]^{1/2}}{\left[\frac{1}{6}\frac{r_p^3}{r_m^3}\frac{V_m}{V_p}\right]^{1/2} - 1} \qquad (1)$$

Unity in the denominator may be neglected in comparison to the value of

$$\left[\frac{1}{6}\frac{r_p^3}{r_m^3}\frac{V_m}{V_p}\right]^{1/2}.$$

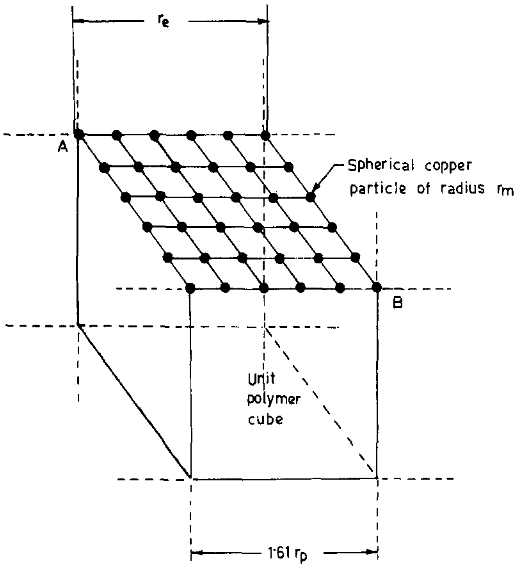
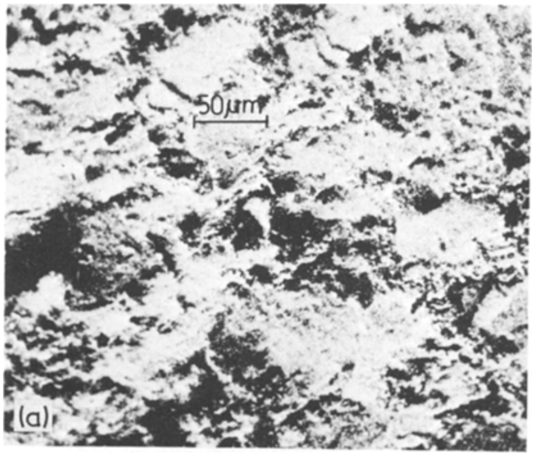


Figure 9 The proposed model of polymer–metal composite with the metallic particles arranged in a square lattice around the polymer phase. (Arrangement is shown only on surface AB, identical arrangements exist for all other surfaces).



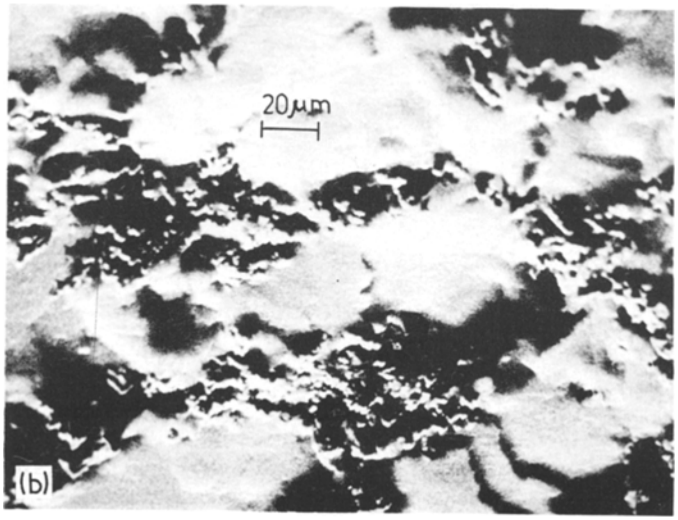


Figure 8 Scanning electron micrograph of the tensile failure surfaces: (a) at 2 vol% metal concentration; (b) at 15 vol% metal concentration.

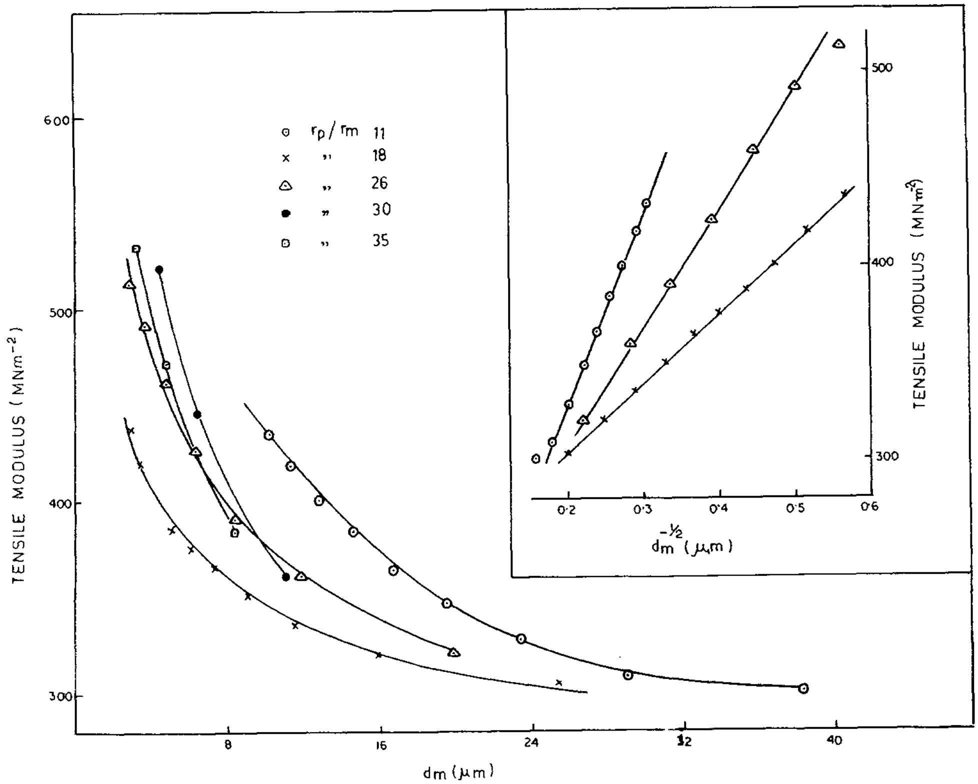


Figure 10 Plot of tensile modulus as a function of d_m for various particle size ratios.

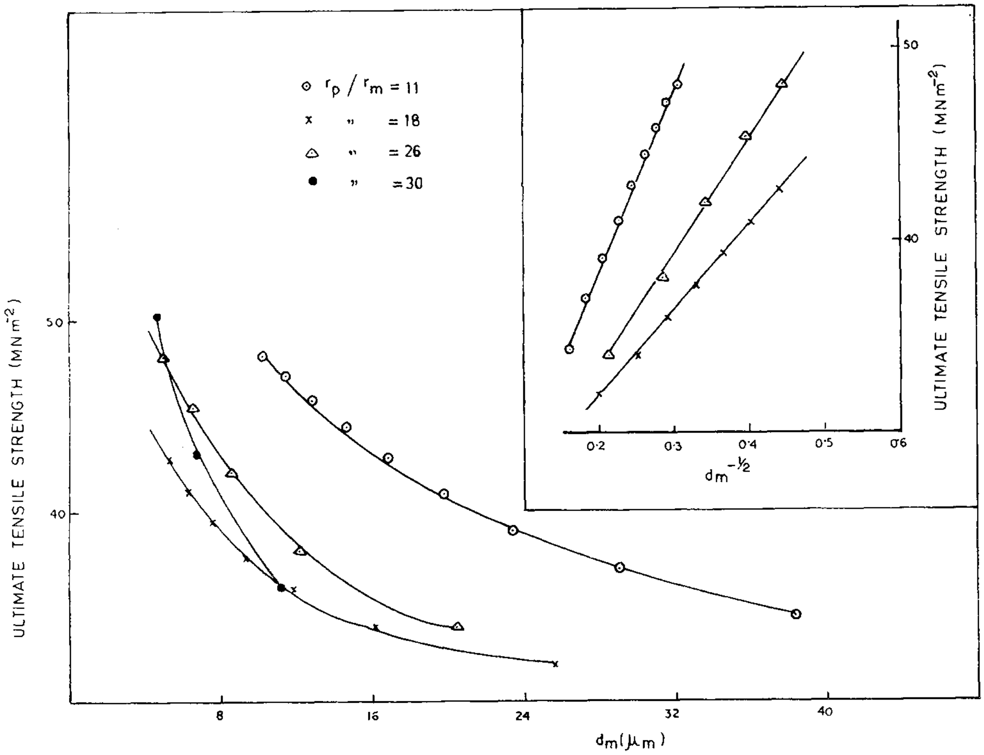


Figure 11 Plot of tensile strength as a function of d_m for different particle size ratios.

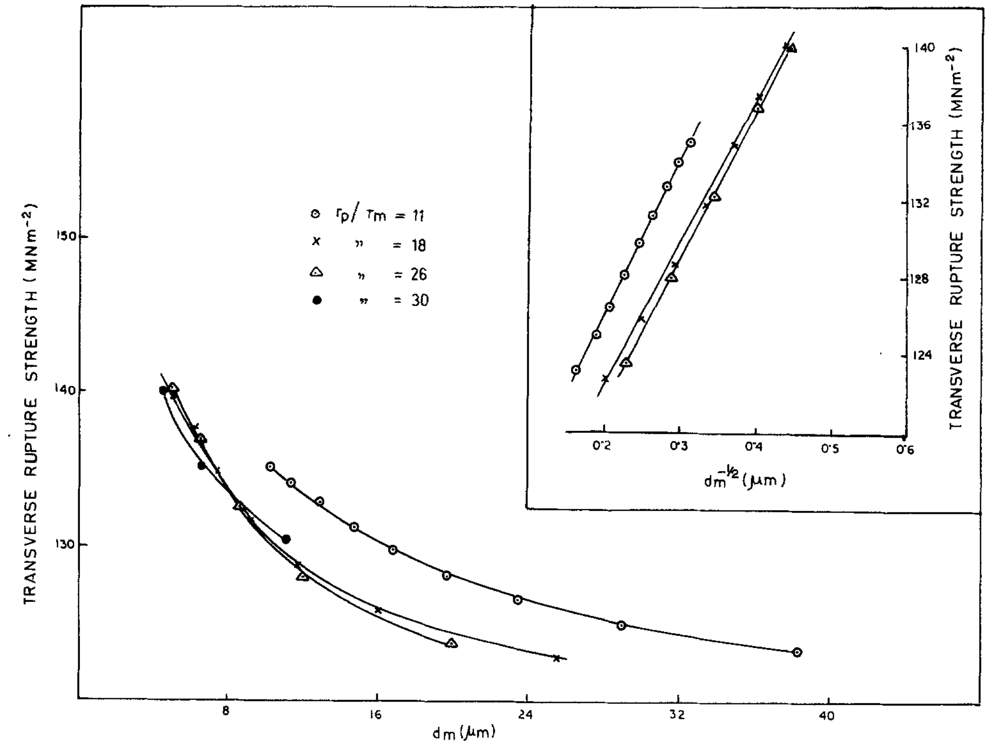


Figure 12 Plot of transverse rupture strength as a function of d_m for different particle size ratios.

r_e can be calculated from the following relation:

$$\frac{V_m}{V_p} = n\frac{r_m^3}{r_p^3}, \qquad (2)$$

$$r_e^3 = \tfrac{4}{3}\Pi(r_p^3 + n\,r_m^3) \qquad (3)$$

Combining Equations 1, 2 and 3

$$d_m = r_m\,[3.95\,(r_p/r_m)^{-1/2}\,V_p^{1/6}\,V_m^{-1/2} - 2] \qquad (4)$$

The values of d_m calculated from Equation 4 are tabulated in Table II and tensile modulus, tensile strength and transverse rupture strength are plotted as a function of d_m in Figs. 10, 11 and 12. Since the model envisages spherical copper particles for the sake of simplicity, the copper particle size has been taken from the result of Fisher's sub-sieve analysis which finds out equivalent particle size in spherical form for any shape of real powder. It is interesting to note from Table II that irrespective of all particle parameters the maximum strengthening occurs in the range of 2 to 4 μm. The absolute value of d_m may be slightly different, since real particle shape has not been considered in the present analysis. However, the point to be stressed here is that the strength maximum is obtained at a particular proximity of particles. Gurland *et al.* [14] in their study of the WC–Co system obtained strength maxima in the mean free path region 0.3 to 0.6 μm. The insets in Figs. 10, 11 and 12 show through some representative data that tensile modulus, tensile strength, transverse rupture strength are inversely proportional to $d_m^{1/2}$, as calculated from the above model. The results reveal that metal particles act as reinforcing fillers up to a particular metal loading. This confirms the earlier indication that the strengthening of the polymer matrix can be achieved by introduction of carbon black and metallic fillers [17, 18]. However, the exact nature of the strengthening mechanism by metallic particles is not clearly understood.

5. Conclusions

(1) Introduction of copper particles in PVC matrix enhances the strength properties up to a particular metal loading, beyond which the strength decreases. At metal loading below the strength maximum fracture propagates through the matrix, while at metal loadings beyond the strength maximum fracture propagates through the segregated metallic particles.

TABLE II Dependence of tensile modulus (TM), ultimate tensile strength (UTS) and transverse rupture strength (TRS) on mean free path of the filler calculated on the basis of the proposed model

% of metal by volume	At $r_p/r_m = 11$				At $r_p/r_m = 18$			
	d_m (μm)	TM × 10^{-2} (MN m^{-2})	UTS × 10^{-1} (MN m^{-2})	TRS × 10^{-2} (MN m^{-2})	d_m (μm)	TM × 10^{-2} (MN m^{-2})	UTS × 10^{-1} (MN m^{-2})	TRS × 10^{-2} (MN m^{-2})
1	59.3	2.90	3.24	1.215	25.5	3.05	3.20	1.230
2	38.3	3.00	3.44	1.235	16.0	3.20	3.40	1.260
3	29.0	3.10	3.70	1.250	11.7	3.35	3.60	1.285
4	23.5	3.28	3.90	1.265	9.2	3.50	3.76	1.320
5	19.7	3.48	4.10	1.280	7.4	3.65	3.94	1.350
6	16.8	3.64	4.28	1.300	6.2	3.75	4.10	1.375
7	14.7	3.84	4.44	1.315	5.2	3.84	4.26	1.395
8	13.0	4.00	4.58	1.325	4.4	4.00	4.25	1.395
9	11.4	4.18	4.70	1.340	3.7	4.18	3.90	1.355
10	10.2	4.34	4.80	1.350	3.1	4.36	3.55	1.310

At $r_p/r_m = 26$				At $r_p/r_m = 30$				At $r_p/r_m = 35$			
d_m (μm)	TM × 10^{-2} (MN m^{-2})	UTS × 10^{-1} (MN m^{-2})	TRS × 10^{-2} (MN m^{-2})	d_m (μm)	TM × 10^{-2} (MN m^{-2})	UTS × 10^{-1} (MN m^{-2})	TRS × 10^{-2} (MN m^{-2})	d_m (μm)	TM × 10^{-2} (MN m^{-1})	UTS × 10^{-1} (MN m^{-2})	TRS × 10^{-2} (MN m^{-2})
20.0	3.20	3.40	1.235	11.2	3.60	3.60	1.28	8.6	3.83	3.90	1.345
12.1	3.60	3.80	1.275	6.6	4.45	4.30	1.35	5.0	4.70	4.50	1.475
8.6	3.90	4.20	1.325	4.6	5.20	5.00	1.40	3.4	5.30	4.50	1.435
6.5	4.25	4.55	1.370	3.4	4.60	4.80	1.38	2.4	4.00	4.20	1.400
5.0	4.60	4.80	1.400	2.2	4.20	4.53	1.36	1.8	3.00	3.85	1.370
3.9	4.90	4.64	1.395	1.9	3.80	4.30	1.34	1.3	–	3.55	1.360
3.1	5.12	4.28	1.370	1.5	3.42	4.00	1.32	0.9	–	3.10	1.290

(2) A model has been suggested to calculate the mean free path between metal particles in the composite. Irrespective of the particle size ratios, maxima in tensile strength, tensile modulus and transverse rupture strength were found to occur at a particular mean free path. This critical mean free path was found to be in the range 2 to 4 μm.

(3) A correlation between strength properties and mean free path has been suggested.

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